State of California

M E M O R A N D U M

To : Henry Voss, Director
Department of Food
& Agriculture
1220 N Street
Sacramento, CA 95814

Date : August 31, 1990

Subject : ARB Monitoring of
Benomyl

From : James D. Boyd
Executive Officer
Air Resources Board

In response to a Department of Food and Agriculture (DFA) request, the Air Resources Board (ARB) staff conducted ambient air monitoring for benomyl resulting from its use as a pesticide. This request was made by the DFA pursuant to Division 7, Chapter 3, Article 1.5, Section 14021 of the Food and Agricultural Code. The monitoring results and additional background information are included in the enclosures to this memorandum.

The benomyl monitoring was conducted in Kern County. Monitoring was conducted to coincide with benomyl applications to almond orchards as a fungicide. Sampling sites were selected after numerous meetings with DFA staff, discussions with representatives of the Agricultural Commissioner's Office of Kern County, and surveys of possible monitoring locations. A chronology of these events is included as Enclosure I.

Four locations were selected as sampling sites. In addition, a background site was selected at Bakersfield. Twenty-four hour samples were collected four days each week from February 8 to March 3, 1988. Short-term samples were also collected downwind of an application of benomyl to an almond orchard. A summary table of the monitoring results is presented in Enclosure II. The complete results are included in Enclosure III.

If you have questions regarding this submittal, please contact me or have your staff contact Genevieve Shiroma, Chief, Toxic Air Contaminant Identification Branch, at 322-7072.

cc: Dr. Michael Lipsett, DHS
William Roddy, Kern Co. APCO
Robert Edwards, Kern Co. Agricultural Commissioner

Enclosures

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Lynn Baker (w/Enclosures)
Pesticides - benomyl file (w/Enclosures)

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING REPORT

Benomyl Monitoring in Kern County

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C88-012

Report Date: May 4, 1990

APPROVED:

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Enclosures to the Transmittal Memorandum on
Benomyl Monitoring Data

August 1990

Enclosure I:	Chronology of Events
Enclosure II:	Summary Table
Enclosure III:	Report on Ambient Concentrations of Benomyl

Enclosure I

Chronology of Events

Benomyl Monitoring
Chronology of Major Events

December 1987	ARB staff discusses benomyl use and sampling locations with representative of Kern County Agricultural Commissioner's Office.
February 1988	DFA transmits to ARB monitoring recommendation for benomyl.
February 1988	ARB prepares work plan for benomyl sampling and analysis.
February 8 - March 3, 1988	Sampling is conducted at Kern County sites.

Enclosure II

Summary Table

Summary Table

Benomyl Pesticide Sampling Study

February, 1988

Station Number	Site	Number of Samples	Samples Above M.D.L. [1/]	Highest Sample Concentration (ppt)	Average [2/] (ppt)
1A [3/]	Pond School	13	None	<6	<MDL
1B [3/]	Pond School	13	None	<6	<MDL
2	Browning School, McFarland	13	2	4	4
3	McFarland Learning Center	13	None	<6	<MDL
4	Wasco High School	13	1	5	5
5 [4/]	ARB Monitoring Sta., Bakersfield	13	1	13	13

Notes:

1/ M.D.L. = Minimum Detection Level = 4-6 ppt for the ambient monitors based on a minimum analytical detection limit of 0.2 ug per sample and an average air sampling volume between 3.7 and 2.7 cubic meters.

2/ Average of samples above M.D.L.

3/ Station 1 was collocated at the district school office in Pond.

4/ Background site.

Enclosure III

Report on Ambient Concentrations of Benomyl

Benomyl Monitoring in Kern County

This report presents the results of ambient benomyl monitoring at different locations in Kern County. The results are based on samples collected and analyzed by the Air Resources Board (ARB) staff using ARB test methods. The results have been reviewed by the staff and are believed to be accurate within the limits of the methods. However, data may have been affected by variables which were not apparent during the test, such as proximity of samplers to the plume after application of the pesticide.

Acknowledgments

The pesticide monitoring study was performed under the direction of David Todd, project engineer, and assisted by Lyle "Bud" Thoma, Instrument Technician. Assistance was provided by Lynn Baker of the ARB Toxic Air Contaminant Identification Branch. Chemical analyses were performed by the ARB Northern Laboratory Branch.

State of California
Air Resources Board

Benomyl Monitoring in Kern County

SUMMARY

The California Department of Food and Agriculture (CDFA) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch requested that the ARB Engineering Evaluation Branch (EEB) conduct ambient monitoring for benomyl (a systemic fungicide) in Kern County during the period of February 8 through March 3, 1988. The monitoring was performed in response to Section 14022(c) of the Food and Agricultural Code, which requires the ARB "to document the level of airborne emissions" when requested by CDFA.

Benomyl is a systemic fungicide used on a wide variety of crops such as almonds, grapes, celery, peaches, citrus, turf, and ornamental flowers and plants. Benomyl is applied by hydraulic-type ground equipment, air-blast sprayers, or aircraft.

Benomyl is not regulated as a restricted pesticide but has produced an increased incidence of tumors in mice. Since it is not a restricted pesticide, statewide Pesticide Use Reports (PUR) only reflect amounts used by licensed pest control operators, aerial applicators, and public agencies. From the 1986 statewide PUR, over 14,800 pounds of benomyl were applied in Kern County in 1986.

The 1986 PUR data were used to determine areas of high use and peak periods of application in Kern County. This information, along with meteorological information, was also used to determine specific locations that are predicted to be impacted by benomyl applications. As a result, four ambient monitoring sites were selected near expected application areas within Kern County. A fifth site was set up in the City of Bakersfield to determine background concentrations. Sampling was conducted to coincide with the peak use of benomyl in the sampling area.

Ambient air samples were collected by using XAD-2 resin tubes as a collection medium for benomyl. Ambient air was drawn through a tube at 2.5 liters per minute (lpm) for approximately 24 hours. Samples were collected at a rate of four samples per week (Monday through Friday) per sample site from February 8 through March 3, 1988.

The sampling and laboratory analysis results are shown in the Summary Table. Benomyl was detected in 4 of the 78 ambient samples. The analytical method's minimum detection level is 0.2 micrograms (ug) per sample, or 4 to 6 parts per trillion (ppt) based on a sampling volume between 3.7 and 2.5 cubic meters.

Summary Table

Benomyl Pesticide Sampling Study

February, 1988

Station Number	Site	Number of Samples	Samples Above M.D.L. [1/]	Highest Sample Concentration (ppt)	Average [2/] (ppt)
1A [3/]	Pond School	13	None	<6	<MDL
1B [3/]	Pond School	13	None	<6	<MDL
2	Browning School, McFarland	13	2	4	4
3	McFarland Learning Center	13	None	<6	<MDL
4	Wasco High School	13	1	5	5
5 [4/]	ARB Monitoring Sta., Bakersfield	13	1	13	13

Notes:

1/ M.D.L. = Minimum Detection Level = 4-6 ppt for the ambient monitors based on a minimum analytical detection limit of 0.2 ug per sample and an average air sampling volume between 3.7 and 2.7 cubic meters.

2/ Average of samples above M.D.L.

3/ Station 1 was collocated at the district school office in Pond.

4/ Background site.

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I. INTRODUCTION

At the request of the California Department of Food and Agriculture (CDFA) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted monitoring for benomyl in Kern County during the month of February, 1988. This study was a coordinated effort between various ARB staff and personnel from CDFA. The monitoring was conducted in accordance with Section 14022(c) of the Food and Agricultural Code, which requires the ARB "to document the level of airborne emissions" when requested by CDFA.

II. PESTICIDE DESCRIPTION

Benomyl is a systemic fungicide, which is an active ingredient in nineteen registered pesticide products. The pesticide may be found in the form of wettable powders, liquids, dusts, or soluble powder. Products containing benomyl are used on a wide variety of crops such as almonds, grapes, celery, peaches, citrus, turf, and ornamental flowers and plants.

Benomyl is not regulated as a restricted pesticide but has produced an increased incidence of tumors in mice. Benomyl has a molecular weight of

290.36. Since it is not a restricted pesticide, only pest control operators and aerial applicators are required by state law to file pesticide use reports with the county. These reports provide the basis of the annual statewide Pesticide Use Report (PUR). Based on the 1986 State PUR, over 14,800 pounds of benomyl were applied in Kern County in 1986. In general, the application rate varies from 0.75 to 1 pound per acre. Benomyl is applied by hydraulic-type ground equipment, air-blast sprayers, or aircraft.

III. SAMPLING LOCATIONS

The 1986 PUR data was used to identify Kern County as an area that had high usage of benomyl and to identify peak periods of application. As a result, four ambient monitoring sites were selected near expected application areas. A fifth ambient monitoring site was set up in Bakersfield to determine background concentrations. Figure 1 shows the study area and the location of each monitoring site. In addition, a sixth site was selected to determine concentrations attributed to a benomyl application. These sites were selected in accordance with the U.S. Environmental Protection Agency ambient monitoring siting criteria (Table 1) outlined in 40 CFR 58. Other considerations in selecting a monitoring site include:

1) proximity of sites to expected application sites,
2) population exposure,
3) reasonable access,
4) availability of electric power, and
5) security.

TABLE 1

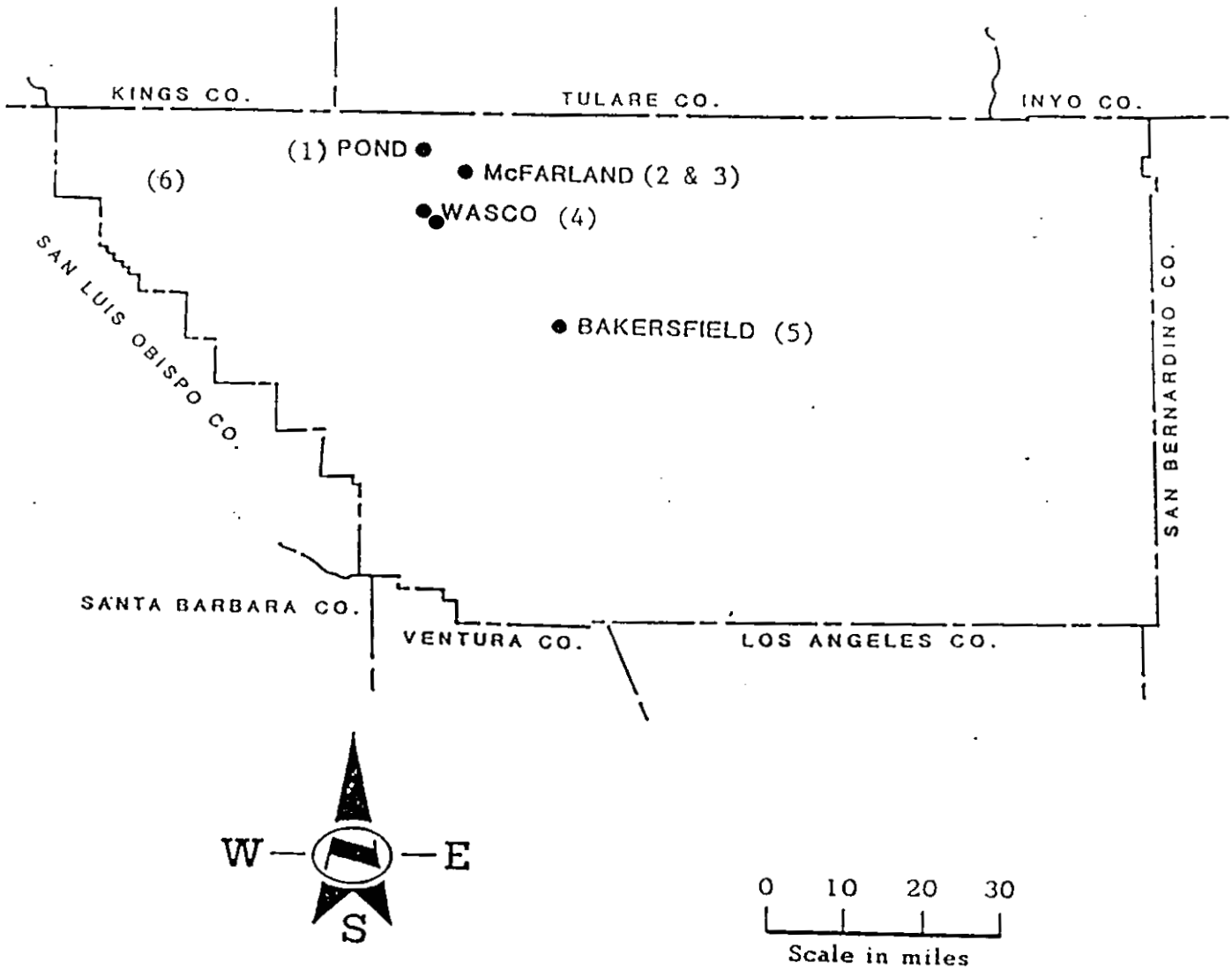
Pesticide Monitor Siting Criteria Summary

Height Above Ground (Meters)	Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	>1	>1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart.

Source: EPA Monitoring Criteria (40 CFR 58)

Figure 1

Pesticide Sampling Sites



Benomyl Sampling Sites
Kern County

Sta. No.	City	Location
1	Pond	Pond School
2	McFarland	Browning School
3	McFarland	McFarland Learning Center
4	Wasco	Wasco High School
5	Bakersfield	ARB monitoring station (background site)
6	Antelope Valley	40 mi. west of McFarland (field applic...

IV. SAMPLING METHODOLOGY

The sampling method used during this study is based on passing measured quantities of ambient air through XAD-2 resin tubes. Any benomyl present in the sampled ambient air is captured by the XAD adsorbent. After the sample was collected, the resin tubes were stored in an iced container until delivered to the ARB's Northern Laboratory Branch in Sacramento for sample recovery and analysis.

Sampling trains designed to collect samples over a twenty-four hour period were set up at each of the five ambient monitoring sites. In addition to these five samplers, another sampler was collocated at sampling site number 1, Pond School.

In general, each week's ambient sampling period began on Monday and ended on Friday. Resin tube changes were made every 24 hours, yielding four samples per week per site. The following schedule is typical of the weekly sampling time frame.

1. Monday A.M. - Travel from Sacramento
2. Monday A.M. to Tuesday A.M. - Sampling Period 1
3. Tuesday A.M. to Wednesday A.M. - Sampling Period 2
4. Wednesday A.M. to Thursday A.M. - Sampling Period 3
5. Thursday A.M. to Friday A.M. - Sampling Period 4
6. Friday P.M. - Travel to Sacramento

The field application monitor was used only for a single field application. Four collocated samples were collected about 25 feet downwind of the field application. The following schedule shows the field application sampling time frame:

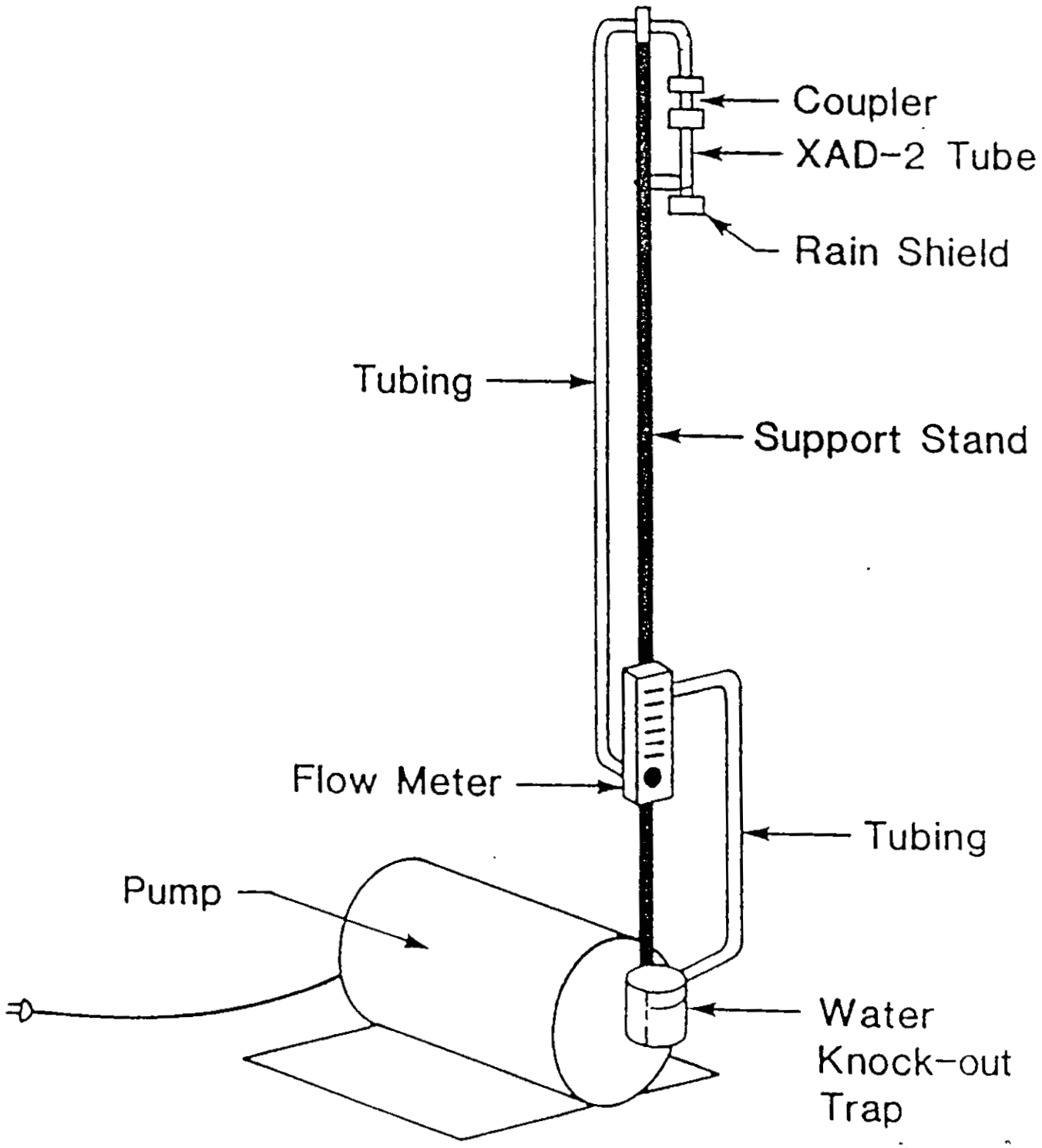
1. 2 hour background sample (before application).
2. 1 hour during field application.
3. 1 hour immediately following field application.
4. 24 hour monitoring which began one hour after the field application.

Each sample train for ambient monitoring and the field application consisted of one XAD-2 resin tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 110 VAC carbon vane pump. (The field application monitor used 12 volt DC pumps instead of the AC pump). A diagram of the sampling train is shown in Figure 2. Each resin tube was prepared for use by breaking off both sealed glass ends and then immediately inserting the tube into a Teflon fitting. The resin tube was oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. The tube was covered to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow adjusted with a metering valve to an indicated flow meter reading of 2.5 liters per minute (lpm) or 1.9

FIGURE 2

PESTICIDE SAMPLING APPARATUS



lpm for the battery powered field application monitor. A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.5 lpm (or 1.9 lpm for the field application). Then the flow, date, time, and site location was recorded in a log.

At the end of each sampling period the final indicated flow rate and the "stop" date and time were recorded. The XAD-2 resin tube was then removed from the sample train, end caps installed on both ends of the tube, and identification labels affixed to each resin tube. Each tube was then stored in a culture tube with a screw cap and stored with ice in a covered ice chest and transported to Sacramento. In Sacramento, the tubes were delivered to the ARB's Northern Laboratory Branch for analysis.

V. ANALYTICAL METHODOLOGY

All samples were analyzed by the ARB's Northern Laboratory Branch, using S.O.P. No. NLB021, Standard Operating Procedure for the Determination of Benomyl and its Breakdown Product, Carbendazim in Ambient Air (see Appendix A). The exposed XAD-2 adsorbent tubes were frozen until desorbed with 2 ml of acetonitrile. Then 50 ul of the acetonitrile solution was injected into a high performance liquid chromatograph for quantitating the benomyl.

VI. RESULTS

Ambient concentrations of benomyl were monitored in Kern County from February 8 through March 3, 1988, with a total of 103 samples taken, including blanks and background samples. Benomyl was detected in only four of the samples--2 from Browning School, 1 from Wasco High School, and 1 from Bakersfield. The minimum detection limit for the ambient samples was between 4 and 6 ppt, based on a minimum analytical detection limit of 0.2 micrograms (ug) per sample and an average air sampling volume of 2.7 to 3.7 cubic meters. All samples with detected amounts of benomyl were near the minimum detection level except the Bakersfield sample. A summary of the results is presented in Table 2. Sampling and analysis data are presented in Appendices B and C.

It is not known why benomyl was detected in the background monitor located in Bakersfield. The monitor was located on the roof of a two story building in a commercial section of the city. The building is also located near a residential section with mature trees and established landscapes. As noted earlier benomyl is not a restricted pesticide and is available to the general public in a number of products such as sprays for roses.

For the field application, benomyl was not detected in any of the field application site samples. The minimum detection limit was 145 ppt for the samples collected during and up to 2 hours after the application in the field. For the sample collected from 3 to 27 hours after the application, the detection limit was 6 ppt.

Table 2

Benomyl Pesticide Sampling Study

February, 1988

Summary of Results

Station Number	Site	Number of Samples	Samples Above M.D.L. [1/]	Highest Sample Concentration (ppt)	Average [2/] (ppt)
1A [3/]	Pond School	13	None	<6	<MDL
1B [3/]	Pond School	13	None	<6	<MDL
2	Browning School, McFarland	13	2	4	4
3	McFarland Learning Center	13	None	<6	<MDL
4	Wasco High School	13	1	5	5
5 [4/]	ARB Monitoring Sta., Bakersfield	13	1	13	13
6	Field Application	4	None	<145	<MDL

Notes:

1/ M.D.L. = Minimum Detection Level = 4-6 ppt for the ambient monitors, based on a minimum analytical detection limit of 0.2 ug per sample and an average air sampling volume between 3.7 and 2.7 cubic meters. The minimum detection level for the field application monitor was 6 to 145 ppt based on the 0.2 ug minimum analytical detection level and sampling volumes between 2.9 cubic meters (for the 24-hour sample) and 0.1 cubic meters (for the 1-hour samples).

2/ Average of samples above M.D.L.

3/ Station 1 was collocated at the district school office in Pond.

4/ Background site.

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A variety of quality control measures (see Appendix D) were taken to check the quality of the data. This includes a flow check of all flow meters by ARB's Quality Assurance Section (see Appendix D). It also includes, from laboratory analysis (see Appendix C), spike recoveries, conversion/collection efficiency, analysis of field blanks, and data precision and completeness.

Based on the flow checks of the flow meters, the correction coefficients for the meters were found to range between .9995 and .9999. Since the correction coefficients round to 1.0 (matching the precision indicated by the meters themselves) no correction was made to any of the flows.

Based on the laboratory results, spike recoveries, where XAD-2 tubes were spiked with benomyl, indicate an 85 to 106 percent recovery. The conversion/collection efficiency study, in which 2.5 liters per minute of air were drawn through spiked samples for 24 hours to simulate sample collection, indicate a 71 to 87 percent recovery. Benomyl was not detected in any of the blanks. Minimum detection level for the blanks was the same for all samples - 2 ug. The results of the various quality control audits were not used to adjust the results listed in Table 2 or the Appendices.

Precision at the collocated Pond sampling site and the field application site can not be calculated because all samples were below the minumum detection limit at those sites. Data completeness for the entire data set was 100% for all samples, based on the number of valid samples analyzed divided by the total number of samples collected.